GRAPHENE DERIVATIVES BASED TRANSPARENT CONDUCTING THIN FILMS FOR OPTOELECTRONIC APPLICATIONS

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1. Introduction

A thin film has a thickness of less than one micrometre and is deposited on a substrate mainly by two methods: chemical vapour deposition (a volatile fluid precursor produces a chemical change on a surface) and physical vapour deposition (a material is released from the source and deposited on a substrate using the mechanical, electrochemical or thermodynamically method). Electronic devices like sensors, solar panels, supercapacitors and numerous other devices are dependent on thin film technology. Emerging thin-film photovoltaic cells such as dye-sensitized solar cells, organic solar cells, and perovskite solar cells are attractive because of the ease of fabrication and the high power-per-weight of the materials compared to silicon solar cells [1][2]. To surpass silicon technology, it is imperative to produce a cost-effective photovoltaic cell. One of the main advantages of organic solar cells is the potentially low price, but indium tin oxide (ITO), a transparent conducting electrode (thin films of optically transparent and electrically conducting material) might be outbalanced by rising transparent conductive oxide costs which is widely used for device fabrications. These are important components in many electronic devices including liquid crystal displays, OLEDs, touch screens, etc. For example, an indium tin oxide (ITO) on polyethylene terephthalate (PET) substrate costs 30% of the material expense [3]. The price of ITO, its brittleness (an issue for flexible devices) and the possible diffusion of indium into organic materials are strong arguments for finding alternative transparent electrode materials. One possible alternative to ITO is aluminium-doped zinc oxide (Al-ZnO). Generally, Al-ZnO has a similar conductivity as ITO, with resistivity's ranging from low $10^{-4}\,\Omega$ cm for pulsed laser deposition to low $10^{-3}\,\Omega$ cm for magnetron sputtering and transmittance of 80-90% in the visible region. However, ZnO is chemically unstable to acid, somewhat brittle and tends to grow with rough surfaces [4]. Furthermore, the desire for greener transparent conducting thin films (TCTs) has prompted the search for alternatives to the present expensive and hazardous indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) electrodes [5][6].

Carbon materials are used in solar cell applications because of their good response to electrical and optical characteristics. Despite their novel qualities, carbon materials are

still not used for commercial applications successfully. To be used economically, there is a need for a better understanding and tuning of the structural, optical and electrical properties of carbon materials which is the key to high-performing devices. Graphene has a transparency of 97.7% per monolayer. This unique optical behaviour combined with its remarkably high electron mobility, high chemical stability, superior mechanical strength and flexibility makes it a top candidate for transparent electrode applications. As an ideal 2D material that can be assembled into electrodes with low roughness and high conductivity, large surface area thin graphene films are often used. However, graphene's low dispersion and weak interface bonding force with the matrix limit its usage [7]. In addition, the large-scale synthesis of high-quality graphene is a concern. Due to the presence of functional groups, graphene oxide (GO), a derivative of graphene, has good solvent dispersion [8]. Moreover, the covalent nature of C–O bonding caused by the presence of functional groups disrupts graphene's sp^2 conjugated hexagonal structure, resulting in non-conducting GO. Nonetheless, conducting reduced GO can be accomplished by incorporating partial reduction of GO and thus restoring an essential electrical characteristic [9]. Several methods have been followed for r-GO synthesis; thermal reduction, hydrothermal method, and microwave irradiation [10]. But these methods are inadequate for large-scale production, hindering practical applications. Hence there is an increasing demand and need for the large-scale production of rGO with a tunable energy band gap. Amongst the rGO synthesis methods, the chemical reductions of oxygen functional group rich GO, synthesized by pristine graphite, is a promising and convenient method. The GO is bonded with functional groups at the basal plane (hydroxyl and epoxide group to sp^3 carbon) and edges (carbonyl and carboxyl group to sp^2 carbon). The active sites on the surface render hydrophilic nature to GO [11]. The chemical reduction favours the large-scale and cost-effective production of r-GO to meet various application requirements. Conventionally, hydrazine and hydrazine derivatives are used to de-oxygenate GO [12]. But their corrosive, highly flammable, and toxic nature hinders their economic use [13]. The rGO prepared using these chemicals renders hydrophobic properties and results in agglomeration of rGO in solvents inhibiting homogeneous dispersion. To deposit rGO transparent conducting thin film by spin coating, dip coating or spray pyrolysis methods, we essentially require a homogeneously dispersed rGO solution. The wide band gap required for transparent conducting thin film is also easily achievable using mild green reducing agents. For resolving the risk involved with the reducing agents, the current research emphasis is on uncovering the effective and ecologically sound-reducing agents for rGO synthesis. Diana N.H *et al.* reported the preparation of rGO by using aspartic acid, wherein GO was sonicated and stirred for several hours [14]. De Silva *et al*. reported the synthesis of rGO using ascorbic acid in

which the time-dependent reduction study was performed [15]. Gulia *et al.,* employed spin coating method for GO deposition and irradiated the thin film of GO by electron. From the current vs. voltage characteristic, they came to a conclusion that conductivity increases with the increasing e-beam irradiation [16]. Hyeon-Jin *et al.,* in their work found that the sheet resistance of graphite oxide film deposited on glass substrate using spin coating method reduced using sodium borohydride ($NaBH_4$) is much lower than that of films reduced using hydrazine (N_2H_4) [17]. Wei *et al.,* in their work, they devised a complete reduction process through chemical conversion by sodium borohydride and sulphuric acid treatment on spin coated thin films, followed by thermal annealing. This method was particularly effective in the restoration of the π-conjugated structure, and led to highly soluble and conductive graphene materials [18]

The chemical method of synthesizing reduced graphene oxide (rGO) includes oxidation of graphite (modified Hummer's method), filtration and then reduction by reducing agents. Spin coating and dip coating methods have been widely used for rGO thin film fabrication. But obtaining a large area of the uniform thin film with desired band gap is still a challenge. Pulsed laser deposition is one of the physical vapour deposition methods which uses high vacuum technology. In literature, Xu *et al.* studied the optical and electrical properties of graphene thin film deposited by KrF laser ablation on quartz, sapphire and n-silicon substrates at 750 ^{o}C [19]. Bhaumik *et al.* have studied the rGO thin film deposited on the SiO_2/Si thin film by using the KrF Excimer laser [20]. The material's energy gap is critical in exhibiting TCT properties. Better electron transfer with maximal transmittance is achievable by instilling a material with a higher electron flow capacity and a wide band gap. Emerging, reliable materials for optoelectronic applications include graphene derivatives with high electrical conductivity and zinc oxide (ZnO) compounds with a wide band gap [21],[22]. Zinc oxide (ZnO), is a well-known transparent, non-toxic, economical, and direct large band gap (3.30 eV) semiconducting oxide for optoelectronic applications. However, the conductivity of ZnO is insufficient to outperform ITO and FTO. Hence the efforts have been made by introducing the layer structured reduced graphene oxide into the ZnO matrix to enhance the electrical conductivity. The composite formation of ZnO with GO efficiently modifies the morphology, band gap and defect states [23]. The incorporation of ZnO with GO could result in a promising heterostructure to improve the optoelectronic device performance. Paul *et al* used isopropanol as a solvent for the GO dispersion and studied the GO: ZnO composite thin film for UV detection [24]. Khorramshahi *et al* studied the Mg-doped ZnO:GO composite for acetic acid-sensing application [25]. Lee *et al.,* in their work, have used rGO-ZnO (reduced graphene oxide – zinc oxide) nanocomposite as an n-

type buffer layer for inverted solar cells and it showed higher electron conductivity than intrinsic ZnO. The addition of rGO, resulted in lower internal resistances, faster electron transport and a lower charge recombination rate, which resulted in a high current density [26].

The low cost and large-area deposition of thin films is a requirement. In addition, utilizing environmentally friendly materials like graphene derivatives needs a better understanding to be used as transparent conducting electrodes. Overall, the study aims the evaluation of the optoelectronic properties of reduced graphene oxide and its composite with metal oxide using different deposition technologies.

Aims and Objectives

From the literature, it is understood that to increase the efficiency of the organic solar cell, the complete collection of photogenerated charge carriers by the corresponding electrode is a crucial point. Also, there is a need for the replacement of conventional transparent conducting electrodes by using eco-friendly and low-cost electrodes. Therefore, different practical approaches are needed to be undertaken to overcome the problem. Thus, in the present research work, the effort is made towards depositing good quality transparent conducting thin film using non-hazardous carbon materials by different deposition technologies.

1. To synthesize GO using improved Hummer's method and deoxygenate the synthesized graphene oxide by environment-friendly reducing agents and investigate the structural, morphological, optical and electrical properties of spin-coated reduced graphene oxide thin films.
2. To deposit rGO thin films on glass substrate by the pulsed laser deposition method and optimize the substrate temperature, the number of laser pulses and oxygen atmospheric pressure to achieve the desired optical and electrical properties.
3. To investigate the structural, optical, and electrical properties of gamma-irradiated rGO thin films.
4. To study the structural, optical, and electrical properties of spin-coated GO:ZnO and GO:Al-ZnO composite thin films.
5. To study the structural, optical, and electrical properties of gamma-irradiated GO: Al-ZnO composite thin films.

A brief sketch of the thesis is as follows:
The thesis consists of six chapters.

Chapter 1: Introduction and Literature Review

This chapter gives an introduction to thin films and their utility in transparent conducting electrodes (TCE) applications. It includes the introduction of carbon materials and their allotropes like graphite, graphene oxide (GO) and reduced graphene oxide (rGO). A brief explanation of the composite of GO with ZnO and Al-ZnO is also included in this chapter. Also, it includes a brief literature survey on the use of these materials for TCT applications. The advantages and disadvantages of using different deposition techniques are discussed. The aim and objectives of the present work are outlined at the end of this chapter.

Chapter 2: Experimental Methods and Characterization Techniques

There's a great demand for low-cost and low-temperature synthesizing methods to get superior thin films for optoelectronic device applications. To control the different properties of thin films, a proper selection of deposition techniques is required. This chapter describes the various thin film deposition methods and their advantages and disadvantages. The principles and instrumentation of the characterization techniques used for the structural (X-ray Diffractometer, Raman Spectroscopy), optical (UV-Vis Spectroscopy, Ellipsometric spectroscopy, photoluminescence spectroscopy), morphological (Field emission scanning electron microscopy), chemical (Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy) and electrical study (current vs. voltage and Hall measurement studies) of the carbon materials and their thin films are explained. In the present study, the sol-gel and PLD methods are chosen for the deposition of rGO and GO:ZnO composite thin films and explained in detail.

Chapter 3: Structural, Optical and Electrical Properties of Green Synthesized Reduced Graphene oxide Thin films

The third chapter describes the GO and rGO synthesis methods. The deposition of the rGO thin film on the glass substrate by the spin coating method and investigations of the optoelectronic properties are also explained.

3.1. Green Reduction of Graphene oxide Using *Syzygium samarangense* (SS) Fruit Extract

The present work deals with the transparent conducting thin film (TCT) of ethanol dispersed *Syzgium samarangense* (SS) fruit extract assisted-reduced graphene oxide and their optoelectronic properties. The reduction of graphene oxide is achieved using non-toxic SS fruit extract and confirmed using X-ray diffraction, UV-Visible spectroscopy, X-ray photoelectron spectroscopy, FTIR, and Raman Spectroscopy. The morphologies are studied using FESEM and atomic force microscopy. We observed a broad peak in XRD indicating the amorphous nature of the synthesized rGO. The obtained I_D/I_G ratio from Raman Spectroscopy is 1.17. Homogeneous dispersion is a prerequisite for deposition using the simple spin coating method. The homogeneous dispersion of synthesized rGO in ethanol was spin-coated on the glass substrate. The rGO based transparent conducting thin film annealed at 400^{o}C exhibited optical transmittance of 90.94% and electrical sheet resistance of 5.72×10^{7} Ω/sq. The high transmittance of rGO with low sheet resistance finds its application in transparent conducting thin film electrodes.

3.2. Green Reduction of Graphene oxide by *Mimosa pudica* Leaf Extract

The present work demonstrates a green route for the simple and cost-effective synthesis of reduced graphene oxide. Treatment of synthesized GO with MP extract has resulted in a stable aqueous dispersion. The reduction is confirmed by X-ray diffraction, UV-Visible spectroscopy, X-ray photoelectron spectroscopy, FT-IR, and Raman Spectroscopy. The morphologies are studied using FESEM and atomic force microscopy. The I_D/I_G ratio corresponding to GO and MP-rGO is 0.92 and 1.03, respectively. The potential reduction that has occurred in GO is due to tannin present in the MP extract. A possible reaction mechanism is proposed for the reduction process. The spin-coated GO and MP-rGO transparent conducting thin films showed a sheet resistance of 1.68×10^{11} Ω/sq and 9.615×10^{6} Ω/sq, respectively; thus, MP-rGO shows a lower sheet resistance compared to GO. MP extract can be a substitute for toxic chemicals used in the reduction of GO. Also, the optoelectronic properties support the synthesized MP-rGO in transparent conducting thin films application and also can be a good candidate for graphene composites.

Chapter 4: Direct Growth of Reduced Graphene oxide-like Thin Films From Graphite Using Pulsed Laser Deposition

The third chapter describes the optimization of rGO thin film on the glass substrate at a lower temperature. Also, the optimized thin film of rGO is studied for its optoelectronic properties after irradiation with a high dosage of gamma radiation. X-ray diffraction, UV-Visible spectroscopy, X-ray photoelectron spectroscopy, FTIR, Raman Spectroscopy, ellipsometric spectroscopy, and FESEM are used for the study of optoelectronic properties.

4.1. Optimization of Substrate Temperature for rGO-like Thin Film Deposition.

One of the major factors which determine the film growth is the substrate temperature. This factor controls the atom mobility on the film surface and thereby determines the physical characteristics of the deposited films such as the optical indices and microstructure. The temperature is a very important deposition parameter that determines the composition and bonding structure between atoms in the deposited carbon films. Normally, the elevated substrate temperature enhances the mobility of surface atoms, causing dissociating of the weak C bonds and the relaxation of the sub planted C atoms, which contributes to the decrease of other contents and the progressive graphitization of the films deposited at a higher temperature. In the present work, the carbon thin films were deposited on a glass substrate by PLD at different temperatures (400 ^{o}C, 500 ^{o}C and 600 ^{o}C). The XRD, UV-Vis spectroscopy, Raman spectroscopy, FESEM and electrical measurements are performed on the thin films at different temperatures. It is observed that at 600 ^{o}C, the thin films showed better electrical properties. During deposition at high temperatures, the carbon atoms have sufficient energy to rearrange themselves to attain thermodynamically stable bonding configurations. With the increase in temperature, the tetrahedral sp^3 transforms gradually into a trigonal sp^2 structure [27].

4.2. Optimization of the Number of Laser Pulses for the Deposition of rGO-like Thin Film.

The thin film of rGO was grown on the glass substrate at a comparatively low temperature of 600 ^{o}C by using pulsed laser ablation in the presence of the oxygen atmosphere and evaluated the optical properties and electrical properties. The thin film of rGO having a transmission% of 95.71 is grown and studied the electrical behaviour by using the current vs. voltage graph. Pulsed laser deposited thin film is optoelectronically

active and it is n-type. Further studies have to be pursued for the effective growth and large scale deposition of rGO thin film for n-type transparent conducting thin film.

4.3. Optimization of Oxygen Pressure in the Ablation Chamber for the rGO-like Thin Film Deposition.

The rGO-like thin film is grown on the glass substrate by a direct growth using the pulsed laser deposition technique at a lower temperature (~ 600 ^{o}C). Investigations on the structural, morphological, optical and electrical properties were performed. The optimized rGO-like thin film showed 87.24% of transmittance. The controlled oxygen atmosphere in the ablation chamber allows the smooth morphology due to the functional group attachment. The functional groups with defects like hexagon are investigated in X-ray photoelectron spectroscopy. The electrical conductivity in the rGO-like thin film is due to the graphene-like layered structure due to the exfoliation by laser ablation. We speculate that the n-type conductivity in the optimized sample is due to the heptagon defects in the structure which are good donors. The highest mobility (18.8589 $cm^2 V^{-1} s^{-1}$) and the transmittance of 87.24% of the rGO-like thin film claim to be a strong candidate for transparent conducting thin film application.

4.4. Effect of Gamma-irradiation on the Optoelectronic Properties of rGO-like Thin Film.

Gamma radiation is widely used in many areas, such as in industry, medicine, military, research and nuclear power production. Gamma radiation emitted from radionuclides such as Cobalt-60 isotope is the most energetic form of electromagnetic radiation. Gamma radiation induces slight changes in the optoelectronic properties of the optimized rGO thin film. The samples were irradiated by γ-radiation at 50 and 75 kGy doses at the rate of 2.519 kGy/hour. The effect of gamma irradiation on the optoelectronic properties of the rGO thin films was studied using XRD, UV-VIS spectroscopy, Raman spectroscopy, FESEM, FTIR and four-probe method for electrical measurements. Irradiation increased the electrical conductivity of the film. But due to the gamma irradiation on the thin film the transparency of the film slightly decreased (Figure 1(a)). The current vs. voltage graph of irradiated thin films shows ohmic nature and is shown in Figure 1(b). Hence, the results show that the gamma-irradiated transparent conducting electrodes thin films can play a crucial role in the solar panels which are used for space applications.

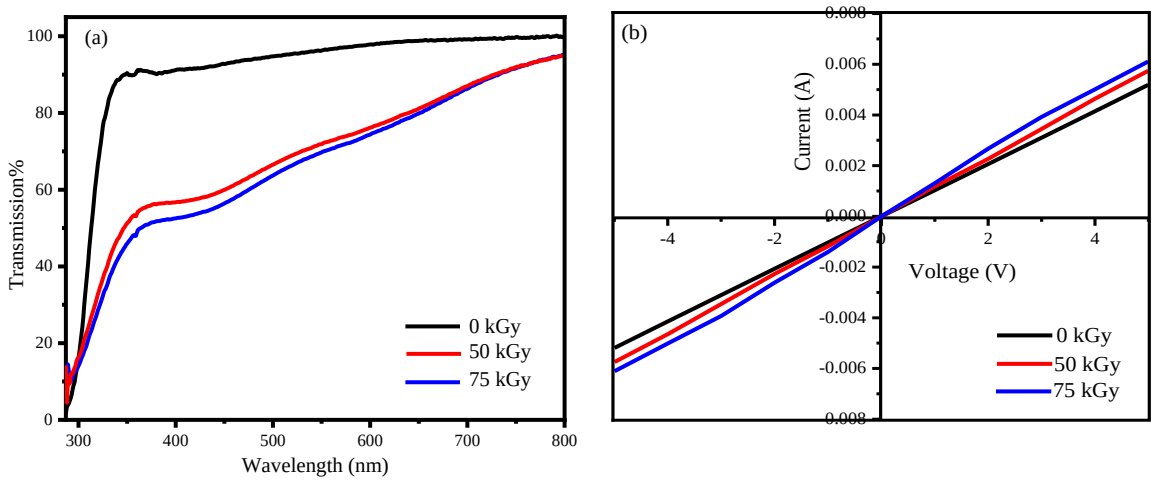

Figure 1: (a) Transmission spectra of un-irradiated and irradiated rGO thin films (b) Current vs. Voltage graph of 0 kGy, 50 kGy, and 75 kGy gamma-irradiated rGO-like thin films.

Chapter 5. Structural, Optical and Electrical Properties of Spin Coated Graphene oxide and Zinc oxide/Aluminium Doped Zinc oxide Composite Thin Films

The third chapter explains the optimization of GO and ZnO/Al-ZnO composite thin film on the glass substrate for different concentrations of GO and optimization of widely used 2-methoxyethanol solvent for thin film deposition. Also, the optimized thin film of GO:Al-ZnO is studied for its optoelectronic properties after irradiation with a high dosage of gamma radiation. X-ray diffraction, UV-Visible spectroscopy, X-ray photoelectron spectroscopy, FT-IR, Raman Spectroscopy, ellipsometric spectroscopy, photoluminescence spectroscopy and FESEM are used for the study of optoelectronic properties.

5.1. Structural, Optical and Electrical Properties of GO:ZnO Composite Thin Films with Different GO Concentartion

ZnO is a promising material for various electronic and energy areas due to its outstanding chemical stability, abundance, non-toxicity, and low cost. However, controlling the electronic transport properties of ZnO by facile strategy is still necessary for wider applications. The thin films of ZnO and eco-friendly synthesized GO composite were deposited on a glass substrate by a simple and cost-effective sol-gel spin coating technique. The transparent and conductive thin films of GO: ZnO composites were deposited on the glass substrate by using 2- methoxyethanol as a dispersing solvent. The

effect of different % of GO in ZnO composite is studied. The analysis of the results reveals the decreased crystallite size in composites compared to pristine ZnO thin film with the increased addition of GO%. The presence of GO sheets results in reduced particle size during the nucleation process. The transmission% decreases with an increase in GO%. The energy gap decreases with GO because reduced GO acts as an anchoring agent and the functional group present in reduced GO helps in charge transfer and results in the intermediate band formation below the conduction band. The morphological studies confirm the decreased particle size. The increase in current with voltage in the I-V study signifies that reduced GO promotes the carrier transformation. The results infer that the incorporation of GO can enhance the conductivity of ZnO thin film, making it suitable for the application in a transparent conducting electrode for solar cells.

5.2. Structural, Optical and Electrical Properties of GO:ZnO Composite Thin Film in Bimixture Solvent with Different GO Concentration.

Graphene oxide sheets were synthesized by an eco-friendly improved Hummer's method. The GO dispersion was optimized using a binary solution of water and 2-methoxyethanol to get a homogeneously dispersed solution for thin film deposition using an easy and cost-effective spin coating method. The TCTs of ZnO and composite with different concentration of GO was deposited on the glass substrate using the optimized binary solution. The effect of different % of GO in ZnO a composite thin film is studied. The structural properties analysis reveals that with GO incorporation the crystallite size decreases in composites compared to pristine ZnO thin film. The GO sheets in the matrix result in reduced crystallite size during the nucleation process. The optical studies suggest a decrease in the transmittance of the composite thin film with an increase in GO%. The narrowing of the energy gap with GO addition is due to the in-situ reduction of GO due to heating and the reduced graphene oxide acts as an anchoring agent and the functional group remained helps in charge transfer and results in the intermediate band formation below the conduction band and thus the energy gap decreases and is evidenced with the photoluminescence results. The direct effect of binary solution for homogeneous dispersion of GO and ZnO is observed in the morphological studies where the uniformity in the particle distribution is obtained in the large surface area. The electrical property studies reveal the decreased sheet resistance with an increase in GO inclusion signifies that reduced GO promotes the carrier transformation and the uniformity of the thin film also enhances the electrical conductivity of the thin film. The results infer that the GO addition and the enhanced homogeneity of the GO:ZnO mixture solution can effectively promote the performance of thin-film for TCT electrode applications.

5.3. Structural, Optical and Electrical Properties of GO:Al-ZnO Composite Thin Film with Different GO Concentrations.

The combination of GO and ZnO showed a decrease in the resistivity of the thin film. As reported in the literature, aluminium doping to ZnO further decreases the resistivity of the ZnO thin film [28]. In the present work, GO is made composite with the aluminium doped zinc oxide (Al-ZnO). GO:Al-ZnO composite thin film with varying concentrations of GO was deposited on the glass substrate by a spin coating method and investigated the electronic transport behaviour. Figure 2 shows the current vs. voltage graph of Al-ZnO and GO:Al-ZnO (15% and 25%) composite thin film. The electron transport in pristine Al-doped ZnO thin film is strongly affected by grain boundary scattering[29]. As the concentration of GO in Al-ZnO thin films increased, the sheet resistance decreased. The decrease in the sheet resistance is due to the decrease in the energy band gap that occurred by the virtue of GO sheets.

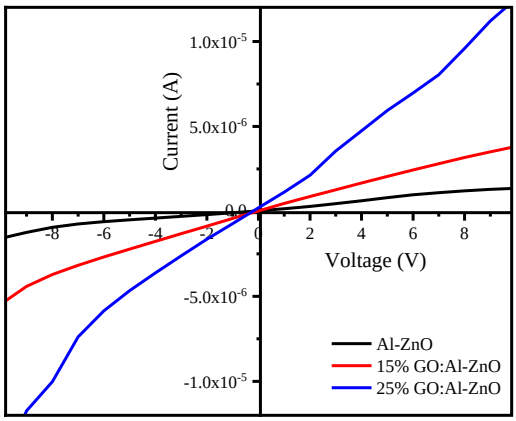

Figure 2. Current vs. voltage graph of Al-ZnO, 15%GO:Al-ZnO and 25%GO:Al-ZnO thin films.

5.4. Structural, Optical and Electrical Properties of Gamma-irradiated GO:Al-ZnO Thin Films

This chapter describes the effect of high dose gamma irradiation on the structural, optical, morphological and electrical properties of GO:Al-ZnO composite thin film deposited on the glass substrate by a spin coating method. For the gamma irradiation study, the prepared thin films were cut into four samples to keep the concentration of the sample the same. Thus, any changes observed in the thin film characteristics are only due to the gamma irradiation. The samples were irradiated by γ-radiation (Cobalt-60 isotope)

at different doses (50 and 75 kGy) at the rate of 2.519 kGy/ hour. Gamma irradiation on Al-ZnO and GO:Al-ZnO (15% and 25% GO) is performed. The FESEM images of GO:Al-ZnO showed a prominent change due to the gamma irradiation on the morphology. The morphological changes after irradiation can be observed in Figure 3. Before irradiation, irregular, circular-shaped grains are observed in the thin film of the GO:Al-ZnO matrix. A 50 kGy radiation dose on the composite thin film results in the formation of the rod-shaped Al-ZnO structure on the rGO layers. The average length of the Al-ZnO rod is 0.90 µm and the average diameter is 0.16 µm. With a further increase in gamma radiation dose to 75 kGy, the rod length is decreased due to the increased defects as a result of degradation by an excess amount of radiation dose.

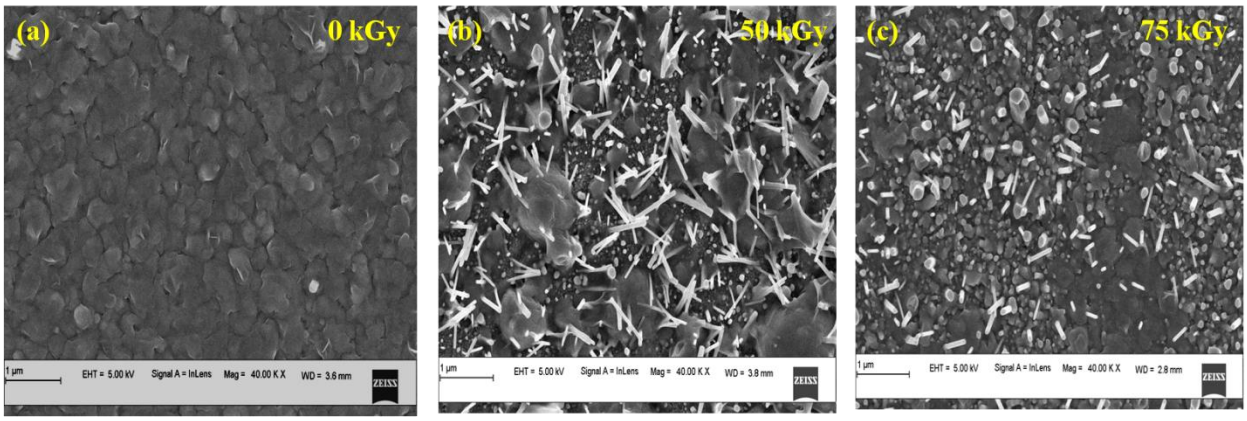

Figure 3: The FESEM images of unirradiated (a) and gamma-irradiated (50 kGy (b) and 75 kGy (c)) GO:Al-ZnO composite thin film.

The electrical behaviour of the spin-coated un-irradiated and irradiated GO:Al-ZnO composite thin film is studied using the four-probe method. The current vs. voltage graph for thin films exhibits ohmic nature and is shown in Figure 4. The sheet resistance decreases for the 50 kGy irradiated thin films. This is because the 50 kGy gamma irradiation results in better crystallinity in the film. But as the dosage increased to 75 kGy sheet resistance increased. The increase in the sheet resistance may be due to the degradation resulting from the gamma irradiation [30].

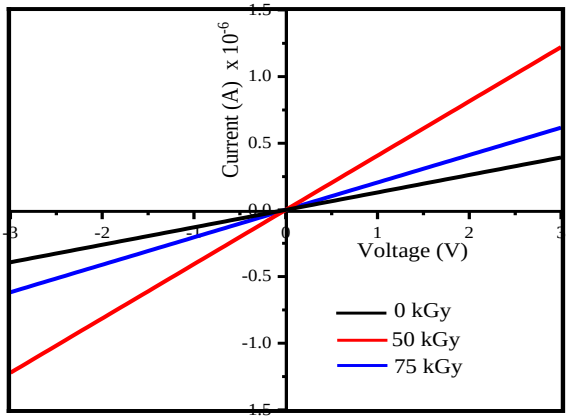

Figure 4: Current vs. voltage graph of 0 kGy, 50 kGy, and 75 kGy gamma-irradiated GO:Al-ZnO thin film.

Chapter 6: Summary and Scope for the Future Work

A comprehensive conclusion of the entire investigations carried out in the present study and the future work plan is presented in this chapter.

- Using toxin-free natural extracts, the *Syzgium samarangense* (SS) fruit and *Mimosa pudica* (MP), the non-conducting GO was reduced to conducting GO (rGO) by an eco-friendly improved Hummers method. The potential of SS and MP extract for the green reduction of GO is established in the present study. The inherent reducing agents present in the SS fruit and MP leaf extract removed the oxygen moieties causing a reduction in the band gap energy of GO. The spin coated thin films of rGO exhibited lower resistivity and higher transmission than the GO thin films. Thus the rGO thin films employed in this study have better potential to be used as a transparent conducting thin film in multilayered optoelectronic devices, and sensors.

- The pulsed laser deposition (PLD), a direct-one step method was employed for the deposition of rGO-like thin film on glass substrate using graphite. The rGO-like thin films are deposited under the optimized deposition parameters such as the substrate temperature, number of pulses ablated on the target, and the atmospheric oxygen pressure. The rGO-like thin films grown on the glass substrate at a substrate temperature of 600 ^{o}C, were highly conductive and optically more transparent. These characteristics of rGO like thin film make it a strong candidate for the replacement of ITO electrodes for optoelectronic applications in solar cells, sensors and LED's.

- For the space application, the effect of irradiation on the thin films becomes important. The rGO-like thin films prepared under optimized deposition conditions were irradiated with the high energy gamma radiation at a different radiation dose of 50 kGy and75 kGy using the cobalt-60 source. The structural, optical, morphological, and electrical properties showed modifications upon irradiation. The transmittance of the rGO-like thin films drastically decreases when subjected to gamma irradiation, however, the sheet resistance of the film decreases with gamma irradiation dosages due to a reduction in GO. The increased I_D/I_G ratio in the irradiated rGO-like thin films compared to unirradiated films indicates the reduction occurred in the film. But the transparency of the film gets affected by the high dosage of gamma-irradiation. The lightweight of the rGO-like materials is an advantage for space applications. Hence, optical and electrical properties reported in the present study for the gamma-irradiated rGO-like thin film are crucial in deciding the applicability for the space application. Previous studies by the researchers have not dealt with the gamma irradiation on rGO-like films and hence the study becomes novel and important for future space application devices like solar cells, sensors and LEDs. But the decrement of transmission% of the thin films on gamma irradiation is the limitation that needs further attention.

- In recent years, composites are gaining interest because the resulting composite matrix possesses the characteristics of the individual composite materials. Although thin films of zinc oxide (ZnO) and aluminium doped zinc oxide (Al-ZnO) are potential candidates to replace ITO films, their electrical conductivity needs further improvement. Hence, the layered structure of graphene oxide is made composite of the ZnO and Al-ZnO material. The sheet resistance of the composite thin film GO:ZnO and GO:Al-ZnO decreased with the increase in the GO%. The inherent deoxygenation that occurred during the final annealing of the thin film results in the formation of reduced graphene oxide layers, and the layered structure formed acts as a network for the flow of electrons. A detailed study was performed on the homogeneous dispersion of GO in 2-methoxyethanol single solvent and 2-methoxyethanol+water bimxtured solvent and its stability over the period were studied. In conclusion, the uniform dispersion of GO is crucial for the enhancement of the optical and electrical properties of the GO:ZnO and GO:Al-ZnO composite thin films. Compared to the optical and electrical properties of the GO:ZnO and GO:Al-ZnO thin films deposited using the single solvents, the bimixtured solvent used in the present study showed better properties. The lower sheet resistance and the increased electrical conductivity upon composite formation suggest the reliability of the

GO:ZnO and GO:Al-ZnO composite thin films for the transparent conducting thin film application in optoelectronic devices like a solar cell, sensor, and LED. The results from the CIE diagrams of the composite films indicate the applicability as a blue phosphor in solid-state lighting (SSL) applications.

- The GO:Al-ZnO thin film was further studied for the gamma irradiation effects for high dosages of 50 and 75 kGy. The electrical conductivity of the 50 kGy gamma-irradiated thin film increased due to increased crystallinity and on further irradiation electrical conductivity decreased due to the degradation of the film. The decreased transparency suggests that the irradiation largely affects the transparency of the film. Previous studies by the researchers have not dealt with the gamma irradiation on GO:ZnO and GO:Al-ZnO film and hence the study becomes novel and important for future space application devices like solar cells, sensors and LED. But the decrement of transmission% of the thin films on gamma irradiation is a limitation that needs further attention.

- The results from the present study show that the direct method of thin film deposition by pulsed laser deposition, a physical vapour deposition method exhibits better electrical and optical properties for the thin films of rGO-like materials on the glass substrate. A higher figure of merit is achieved for the rGO-like thin films deposited by the PLD method compared to the solution-based spin coating methods. Also, the enhancement in the electrical and optical properties of zinc oxide and aluminium doped zinc oxide upon composite formation with graphene oxide suggests that the graphene derivative-based materials play an important role in replacing the toxic indium tin oxide materials. The results in the present study show the potential of carbon materials, particularly graphene derivative-based materials for transparent conducting thin film application. Thus, the results obtained in this study open new routes for the fabrication of cost-effective and good quality thin films for optoelectronic applications using non-toxic and low-cost carbon materials.

Future Scope:

- Graphene oxide and zinc oxide composite thin film can be deposited on substrates by pulsed laser deposition method and the optoelectronic properties may be investigated for their application as a transparent conducting electrode in solar cell and sensor devices.

- ❖ Graphene oxide and other metal oxides like titanium dioxide and zinc sulfide composites may also be deposited on transparent and flexible substrates and may be investigated for their transparent conducting electrode applications in devices like solar cells and sensors.
- ❖ Graphene oxide and metal oxide (TiO_2/ZnO/ZnS) composite thin film may be irradiated by an electron beam and studied for optoelectronic properties. A study on the electron beam irradiation on the thin films is crucial for the space application, wherein they become an important layer in different multilayered devices like transistors, solar cells, and optoelectronic sensors.
- ❖ Graphene oxide and zinc oxide composite thin films may be deposited on flexible substrates and optoelectronic properties may be studied for the application in the flexible transparent solar panels for windows.

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Research articles published in Journals (Peer-Reviewed)

1) **Veena Shivadas Kindalkar**, Sandeep K. M, Kumara K, S M Dharmaprakash, Sol-gel synthesized spin-coated GO: ZnO composite thin films: Optical, structural and electrical studies, *Materials Research Express*, 6, (2019) 096435. (Impact Factor: 1.620)

2) **Veena Shivadas Kindalkar**, P Kumar, C. H. Shraddha, K. Ananya, and S. M. Dharmaprakash Evaluation of optoelectronic properties of Nd: YAG laser deposited rGO thin film for n-type transparent electrode applications, *AIP Conference Proceedings*, 2265, (2020) 124224.

3) **Veena Shivadas Kindalkar**, Kumara K, Shreesha Bhat, Sampyady Medappa Dharmaprakash, An eco-friendly approach for the reduction of graphene oxide using

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4) K. Kumara, **Veena Shivadas Kindalkar**, Felcy Jyothi Serrao, T Chandra Shekhara Shetty, P. S. Patil, S. M. Dharmaprakash, Enhanced nonlinear optical absorption in defect enriched graphene oxide and reduced graphene oxide using continuous-wave laser z-scan technique, *Materials Today: Proceedings*, (2022).

5) Prasad Kumar M. Parvathy Venu, Sandeep Kannaiah, **Veena Shivadas Kindalkar**, M. Ananya Kote, Sampyady Dharmaprakash, Non-polar a-plane oriented ZnO: Al thin films for optoelectronic applications, *Physica B Condensed Matter* 606, 412721, (2021). (Impact factor: 2.436)

6) **Veena Shivadas Kindalkar** and S M Dharmaprakash, Transparent conducting thin films of green synthesized reduced graphene oxide: optoelectronic properties. (Under communication)

Conference/symposium Presentations

1) **Veena Shivadas Kindalkar**, Shreesha Bhat, K. Kumara, Sandeep K. M., Parvathy Venu M., Prasad Kumar and S. M. Dharmaprakash, "Sol-Gel Synthesized Spin Coated GO: ZnO Composite Thin films: Optical, structural And Electrical Studies", presented a poster in 3rd International Conference on "Recent Advances in Material Chemistry" (ICRAMC-2019) held in SRM Institute of Science and Technology, TamilNadu during 13-15 February 2019.

2) **Veena Shivadas Kindalkar**, Prasad Kumar, Ananya Kote and S. M. Dharmaprakash, "Fabrication of Carbon thin films at different oxygen atmospheric pressure by Pulsed Laser Deposition and studies on transparent conducting properties", presented a poster in "International Conference on Advanced Functional Materials for Energy, Environment and Health Care" (AFMEEHC) held on 18-20 March 2019 in Mysore University, Mysore.

3) **Veena Shivadas Kindalkar**, Prasad Kumar, Ananya Kote and S. M. Dharmaprakash, "Evaluation of optoelectronic properties of Nd: YAG Laser deposited rGO thin film for n-type transparent electrode applications", presented a paper in 64th DAE Solid

state physics Symposium on December 18-22, 2019 held at Indian Institute of Technology Jodhpur.

4) K. Kumara, K. V. Anil Kumar, Prasad Kumar, **Veena Shivadas Kindalkar** and S.M. Dharmaprakash, presented a poster entitled "A high quantum yield luminescent N doped reduced graphene oxide by decomposition of Citric acid and Urea" in National Conference on "Nanomaterials for Biomedical Applications" (NBA-2017) on March 16, 2017, at Dental college auditorium, Yenepoya University, Mangalore.

5) **Veena Shivadas Kindalkar**, T Chandra Shekhara Shetty and S. M. Dharmaprakash, "Environmental friendly method for synthesizing reduced graphene oxide for transparent conducting thin film application" presented an oral presentation in 16th Kannada Vijnana Sammelana on September 15-17, 2021 held at Mangalore University. (Received best oral presentation award)

6) Prasad Kumar, K. M. Sandeep, Parvathy Venu M., **Veena Shivadas Kindalkar**, Ananya Kote M., and S. M. Dharmaprakash, "Optoelectronic Properties of Al Doped ZnO Thin Films Fabricated Using Laser Wavelength Dependent PLD Technique for Window Layer Applications", International Conference on "Advanced Materials" held on June 12-14 June 2019 held at Nirmalagiri College, Kannur, Kerala.

7) Prasad Kumar, Parvathy Venu M, Sandeep K M, **Veena Shivadas Kindalkar**, S M Dharmaprakash, "Influence of Target to Substrate Distance on the Structural, Morphological and Optical properties of Al-doped ZnO Thin film prepared by Pulsed Laser Deposition Technique", "International Conference on Recent Advances in material chemistry "(ICRAMC-2019) during 13-15 February in SRM University, Chennai.

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